

October 22, 2004

## Claims

1. Pseudoplastic aqueous dispersions comprising particles (P) which are solid and/or of high viscosity, are dimensionally stable under storage and application conditions, are in dispersion in a continuous aqueous phase (W), and comprise surface-modified nanoparticles (N) whose surface is covered fully or almost fully by
- (G1) modifying groups which
- are attached covalently to the surface via functional linker groups (a) and
  - comprise inert spacer groups (b) and
  - comprise functional reactive groups (c) which are attached via the groups (b) to the groups (a) and are inert toward the functional reactive groups of the surface to be modified, and
- (G2) modifying groups which
- are attached to the surface via functional linker groups (a) containing at least one silicon atom,
  - comprise inert groups (e), and
  - have a smaller hydrodynamic volume  $V_H$  than the modifying groups (G1).
2. Pseudoplastic aqueous dispersions as claimed in claim 1, characterized in that the surface of the nanoparticles (N) is additionally covered by
- (G3) modifying groups which

- are attached covalently to the surface via at least one functional linker group (a) and
- comprise at least one inert group (d) which is attached to the surface via the group (a) and has a smaller hydrodynamic volume  $V_H$  than the inert spacer group (G1b).

3. Pseudoplastic aqueous dispersions as claimed in claim 1 or 2, characterized in that the hydrodynamic volume  $V_H$  can be determined by means of photon correlation spectroscopy or can be estimated from the relationship

$$V_H = (r_{\text{cont}}/2)^3,$$

in which  $r_{\text{cont}}$  is the effective contour length of a molecule.

4. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 3, characterized in that the functional reactive groups of the surface to be modified are hydroxyl groups.
5. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 4, characterized in that the functional linker group (G1a) contains at least one silicon atom.
6. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 5, characterized in that the inert spacer group (G1b) is an at least divalent organic radical R.
7. Pseudoplastic aqueous dispersions as claimed in any one of claims

1 to 6, characterized in that the functional reactive group (G1c) can be activated thermally and/or with actinic radiation.

- 5 8. Pseudoplastic aqueous dispersions as claimed in claim 7, characterized in that the thermally activatable functional reactive group (G1c) is a blocked isocyanate group and the functional reactive group (G1c) which can be activated with actinic radiation is selected from the group consisting of groups containing at least one carbon-carbon multiple bond.
- 10 9. Pseudoplastic aqueous dispersions as claimed in any one of claims 2 to 8, characterized in that the functional linker group (G3a) is selected from the group consisting of ether, thioether, carboxylate, thiocarboxylate, carbonate, thiocarbonate, phosphate, thiophosphate, phosphonate, thiophosphonate, phosphite, thiophosphite, sulfonate, amide, amine, thioamide, phosphoramidate, thiophosphoramidate, phosphonamide, thiophosphonamide, sulfonamide, imide, hydrazide, urethane, urea, thiourea, carbonyl, thiocarbonyl, sulfone, and sulfoxide groups.
- 20 10. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 9, characterized in that the inert group (G3d) and the inert group (G2e) are monovalent organic radicals  $R^2$ .
- 25 11. Pseudoplastic aqueous dispersions as claimed in claim 10, characterized in that the monovalent organic radicals  $R^2$  are selected from the group consisting of aliphatic, cycloaliphatic, aromatic, aliphatic-cycloaliphatic, aliphatic-aromatic, cycloaliphatic-aromatic or aliphatic-cycloaliphatic-aromatic radicals.

12. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 10, characterized in that the inert groups (G1b), (G2e) and (G3d) contain at least one at least divalent functional group and/or at least one substituent.
- 5
13. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 12, characterized in that the surface-modified nanoparticles (N) are preparable by reacting the functional reactive groups of the surface of nanoparticles (N') for modification with
- 10
- (M1) at least one modifier comprising
- at least one functional reactive group (M1a) which is reactive toward the functional reactive groups of the surface to be modified,
  - 15 - at least one inert spacer group (G1b), and
  - at least one functional reactive group (G1c) which is attached to the group (M1a) via the group (G1b) and which is inert toward the functional reactive groups of the surface to be modified, and
  - 20
- (M2) at least one modifier having a smaller hydrodynamic volume  $V_H$  than the modifier (M1) and comprising
- 25 - at least one functional reactive group (M2a) which contains at least one silicon atom and is reactive toward the functional reactive groups of the surface to be modified, and
  - at least one inert group (G2e).
  - 30

14. Pseudoplastic aqueous dispersions as claimed in claim 13, characterized in that the surface-modified nanoparticles (N) are preparable by additionally reacting the functional reactive groups of the surface of nanoparticles (N') for modification with

5

(M3) at least one modifier comprising

10

- at least one functional reactive group (M3a) which is reactive toward the functional reactive groups of the surface to be modified, and
- at least one inert group (G3d) having a smaller hydrodynamic volume  $V_H$  than the inert spacer group (G1b).

- 15 15. Pseudoplastic aqueous dispersions as claimed in claim 13 or 14, characterized in that the modifier (M1) is selected from the group consisting of silanes of the general formula II:

20



in which the indices and variables are defined as follows:

25

m and n are integers from 1 to 6;

o is 0, 1 or 2;

G1c is a group which can be activated thermally and/or with actinic radiation, as defined above;

30

R is an at least divalent organic radical, as defined above;

$R^2$  is a monovalent organic radical, as defined above; and

$R^3$  is a hydrolyzable atom or hydrolyzable group.

5

16. Pseudoplastic aqueous dispersions as claimed in claim 15, characterized in that the hydrolyzable atom  $R^3$  is selected from the group consisting of hydrogen, fluorine, chlorine, and bromine atoms and the hydrolyzable group  $R^3$  from the group consisting of hydroxyl groups and monovalent organic radicals  $R^4$ .

10

17. Pseudoplastic aqueous dispersions as claimed in claim 16, characterized in that the monovalent organic radical  $R^4$  is selected from the group consisting of groups of the general formula III:

15



in which the variable Y is an oxygen atom or a carbonyl group, carbonyloxy group, oxycarbonyl group, amino group  $-NH-$  or secondary amino group  $-NR^2-$  and the variable  $R^2$  is as defined above.

20

18. Pseudoplastic aqueous dispersions as claimed in any one of claims 13 to 15, characterized in that the silanes (M1) of the general formula II are obtainable by

25

- (1) reacting polyisocyanates with blocking agents and with silanes of the general formula IV:

30



in which the variable Z is an isocyanate-reactive functional group and the variables R, R<sup>2</sup> and R<sup>3</sup> are as indicated above; or

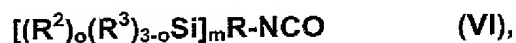
5

(2) reacting compounds of the general formula V:



10

in which the index n and the variables G1c, R and Z are as indicated above, with silanes of the general formula VI:

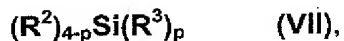


15

in which the index m and the variables R, R<sup>2</sup> and R<sup>3</sup> are as indicated above.

19. Pseudoplastic aqueous dispersions as claimed in any one of claims 13 to 18, characterized in that the modifier (M2) is selected from the group consisting of silanes of the general formula VII:

20



25

in which the index p = 1, 2 or 3 and the variables R<sup>2</sup> and R<sup>3</sup> are as defined above.

20. Pseudoplastic aqueous dispersions as claimed in any of claims 14 to 19, characterized in that the modifier (M3) is selected from the group consisting of hydroxyl-containing compounds of the general formula VIII:

30



in which the variable  $R^2$  is as defined above.

- 5 21. Pseudoplastic aqueous dispersions as claimed in claim 20, characterized in that the hydroxyl-containing compounds of the general formula VIII are primary aliphatic alcohols.
- 10 22. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 21, characterized in that the nanoparticles (N') for modification are selected from the group consisting of metals, compounds of metals, and organic compounds.
- 15 23. Pseudoplastic aqueous dispersions as claimed in claim 22, characterized in that the metals are selected from main groups three to five and transition groups three to six and also one and two of the periodic table of the elements and also from the lanthanides.
- 20 24. Pseudoplastic aqueous dispersions as claimed in claim 22 or 23, characterized in that the compounds of the metals are oxides, oxide hydrates, sulfates, hydroxides or phosphates.
- 25 25. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 24, characterized in that the surface-modified nanoparticles (N) are preparable by reacting the nanoparticles (N') for modification in a first process stage with at least one modifier (M1) and in a second process stage with at least one modifier (M2).
- 30 26. Pseudoplastic aqueous dispersions as claimed in claim 25,



characterized in that the surface-modified nanoparticles (N) are preparable by reacting the nanoparticles (N') for modification in the first process stage with a modifier (M1) and also

- 5        -        in the second process stage with at least one modifier (M3) and in the third process stage with at least one modifier (M2), or
- in the second process stage with at least one modifier (M2) and in the third process stage with at least one modifier (M3),
- 10       or
- in the second process stage with at least one modifier (M2) and with at least one modifier (M3).

27.    Pseudoplastic aqueous dispersions as claimed in claim 25 or 26,  
15       characterized in that the modifiers (M1) and (M2) and also, where used, (M3) are employed in an amount which is sufficient for the full or almost full coverage of the surface of the nanoparticles (N') for modification.

20    28.    Pseudoplastic aqueous dispersions as claimed in any one of claims 15 to 21, characterized in that the surface-modified nanoparticles (N) are preparable by subjecting at least one modifier (M1) of the general formula II and at least one modifier (M2) of the general formula VII to joint hydrolysis and condensation.

25       29.    Pseudoplastic aqueous dispersions as claimed in claim 28, characterized in that the surface-modified nanoparticles (N) are preparable by additionally reacting the resultant surface-modified nanoparticles (N) with at least one modifier (M3).

30

30. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 29, characterized in that the dimensionally stable particles (P) comprise the surface-modified nanoparticles (N) in an amount of from 1 to 40% by weight, based on (P).
- 5 31. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 30, characterized in that the dimensionally stable particles (P) comprise at least one polymeric and/or oligomeric binder.
- 10 32. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 31, characterized in that it comprises in the dimensionally stable particles (P) and/or in the aqueous phase (W) at least one additive selected from the group consisting of crosslinking agents, color and/or effect pigments, organic and inorganic, transparent or
- 15 opaque fillers, other nanoparticles different than the surface-modified nanoparticles (N), reactive diluents, UV absorbers, light stabilizers, free-radical scavengers, devolatilizers, slip additives, polymerization inhibitors, photoinitiators, initiators of free-radical or cationic polymerization, defoamers, emulsifiers, wetting agents,
- 20 dispersants, adhesion promoters, leveling agents, film-forming auxiliaries, rheology control additives (thickeners), flame retardants, siccatives, dryers, antiskinning agents, corrosion inhibitors, waxes, and flatting agents.
- 25 33. Pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 32, characterized in that it comprises the dimensionally stable particles (P) in an amount of from 5 to 70% by weight, based on the pseudoplastic aqueous dispersion.
34. A process for preparing pseudoplastic aqueous dispersions as

- 5 claimed in any one of claims 1 to 33, characterized in that it comprises mixing at least one dispersion (D) of surface-modified nanoparticles (N) whose surface is covered fully or almost fully by modifying groups (G1) and modifying groups (G2) in an aprotic, liquid, organic medium (O) with the remaining constituents of the dimensionally stable particles (P) and dispersing the resultant mixture (P) in an aqueous phase (W) so as to give the dimensionally stable particles (P).
- 10 35. The process as claimed in claim 34, characterized in that the surface of the surface-modified nanoparticles (N) is additionally covered by modifying groups (G3).
- 15 36. The process as claimed in claim 34 or 35, characterized in that the aprotic, liquid, organic medium (O) comprises or consists of at least one aprotic organic solvent and/or at least one reactive diluent.
- 20 37. The process as claimed in claim 36, characterized in that the aprotic organic solvents and/or reactive diluents, in terms of the modifying groups (M1) and, where used, (M3), have a Flory-Huggins parameter  $\chi > 0.5$ .
- 25 38. The process as claimed in any one of claims 34 to 37, characterized in that the dispersion (D) has a surface-modified nanoparticle (N) content of at least 30% by weight.
- 30 39. The use of the pseudoplastic aqueous dispersions as claimed in any one of claims 1 to 33 or of the pseudoplastic aqueous dispersion prepared by the process as claimed in any one the of claims 34 to 38 as a coating material, adhesive or sealant for

producing an opaque or transparent coating, adhesive layer or seal.